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Electrical Conductivities of Polycondensed Benzopyrazine and Related Compounds.

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Abstract

4,5-Dichlorocyclohexene-3,6-dione [I] reacted with ammonia to yield polycondensed heteroaromatic compounds in which benzene rings should fuse alternatively with dihydropyrazine rings. When the reaction time was prolonged, the reaction product was infusible black-brown powder. The powder was dehydrogenated with various oxidizing reagents to accomplish an aromatic character of the molecule. From the product obtained by the dehydrogenation, molecular complexes with iodine, in which the amount of iodine was varied, and chelate compounds of various kind of metal were derived. The electrical resistivities of the reaction product between [I] and ammonia, of the dehydrogenated product, of metal chelate compounds and of molecular complexes of iodine were of the order of $10^{11}\sim 10^{16}$, $10^{13}\sim 10^{14}$, $10^{12}\sim 10^{13}$, and $10^7\sim 10^8$ ohm-cm, respectively.

I. Introduction

It was reported by Akamatu, Inokuchi¹⁾ and many others²⁾ that polycondensed aromatic hydrocarbons and heterocyclic aromatic compounds have an electrically semiconducting property. In this paper, it was aimed to prepare highly condensed polycyclic heteroaromatic compounds with a simple synthesizing method, and to investigate the electrical conductivities of the compounds obtained. As known already, α -halogeno-ketone reacts with ammonia to yield dihydropyrazine with ease. If a molecule has two pair of α -halogeno-ketone groups, the compound must yield a highly condensed polycyclic compound as the result of the reaction with ammonia. As expected, 4,5-dichlorocyclohexene-3,6-dione [I] yielded infusible black-brown powder after prolonged heating with ammonia. However, as the powder obtained could not have a perfect aromaticity probably, the powder was dehydrogenated with various kind of oxidizing reagents.

The electrical resistivity of phthalocyanine was improved a little by a formation of metal chelate compound.³⁾ And complexes of polycyclic aromatic hydrocarbons with halogens have excellent electrical conductivities, as reported by Akamatu and Inokuchi.⁴⁾ Various metal chelates and halogeno-complexes of the powder obtained above and of the dehydrogenated compounds were prepared with an expectation of improved electrical conductivity.

II. Experimental

4, 5-Dichlorocyclohexene-3, 6-dione. — (a) Using chloroform as a solvent: This compound was prepared with the method reported in the literature⁵⁾ with an yield of

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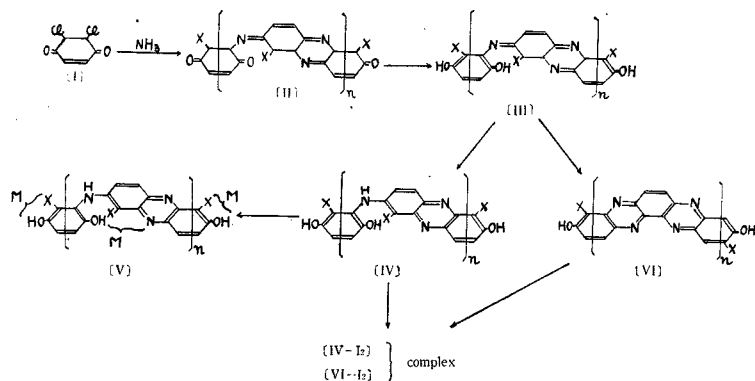


Fig. 1. X: -Cl or -NH₂

62% as a colorless crystals (m. p. 145 ~ 146°C). (b) Using acetic acid as a solvent: Dry chlorine gas was bubbled into a solution of benzoquinone (8.5 g.) in 85 ml. of acetic acid for about forty minutes at 16 ~ 25°C. A yellow solution became gradually colorless, and then colorless powder precipitated out. The precipitate obtained was collected by filtration, washed with ether, and recrystallized from chloroform to obtain colorless crystals (m. p. 146°C). The yield was 9.2 g. (60%). (c) Ninety grams of sulfuryl chloride were dropped in a solution of hydroquinone (25 g.) in 340 ml. of dry ether at 0 ~ 5°C. After stirring for about three hours, the precipitate obtained was collected by filtration, and recrystallized from chloroform to obtain colorless crystals (m. p. 143 ~ 145°C). The yield was 7 g. (19%).

Reaction of 4,5-dichlorocyclohexene-3,6-dione [1] with ammonia.— Thirty five grams of [I] were dispersed in 120 ml. of ethanol and dry ammonia was bubbled gradually with stirring at room temperature. [I] was entered into a solution gradually with successive bubbling of ammonia, and the solution became brown. After bubbling for 3 hours, the precipitate obtained was collected by filtration, washed with hot water and dried in vacuo, to obtain 20 g. of infusible black-brown powder, [III]. (*Anal.* Found ; Cl, 11.4 ; N, 10.6). The ethanol in the filtrate was distilled out and 5 g. of black-brown powder was obtained as the residue.

Reaction of [III] with ammonia.— (a) In dimethylformamide: Dry ammonia gas was bubbled to a solution of 0.5 g. of [III] in 7 ml. dimethylformamide under refluxing for seven hours. After refluxing for additional six hours without bubbling of ammonia, the precipitate obtained was filtered while hot. The precipitate collected was boiled twice with each 100 ml. of distilled water, and was dried under 20 mm. Hg vacuo at 60°C. Infusible black powder (0.4 g.) was obtained. (*Anal.* Found ; Cl, 5.08). The black-brown reaction liquid was poured into water, and a little of black powder was obtained. (*Anal.* Found ; Cl, 9.00). (b) One half gram of [III] was dissolved in 7 ml. of dimethylformamide saturated by ammonia, and was heated at 200 ~ 210°C for twelve hours. The precipitate obtained was collected with filtration, rectified with the methods described above, dried in vacuo. Four tenth grams of

infusible black powder being insoluble in any solvent were obtained. (*Anal.* Found ; Cl, 2.3 ; N, 15.5)

Dehydrogenation with N-bromosuccinimide. — A half gram of [III], 0.7 g. of N-bromosuccinimide, and 0.01 g. of benzoyl peroxide were dissolved in 5 ~ 10 ml. of dimethylformamide, and refluxed for an hour. After cooling, 3 g. of potassium acetate and 1 ml. of acetic acid were poured into the reaction mixture, and again refluxed for an hour. After cooling, the precipitate obtained was filtered, boiled three times with each 100 ml. of distilled water for a half an hour, washed with water-dimethylformamide, and dried in vacuo. Two tenth grams of infusible black powder were obtained. (*Anal.* Found ; Cl, 6.9 ; N, 10.73).

Dehydrogenation with chloranil. — One gram of [III] was suspended in the solution of 2 g. of chloranil in toluene, refluxed for fifteen hours. After filtering, the precipitate obtained was refluxed three times in each 30 ml. of benzene for a half an hour, filtered, and dried in vacuo. Nine tenth grams of infusible black-brown powder were obtained.

Dehydrogenation with lead peroxide. — A half gram of [III] and 20 ml. of acetic acid were dissolved in 10 ml. of dimethylformamide, and to the mixture was added 0.1 g. of lead peroxide. After refluxing for eight hours, the black precipitate obtained was heated in dilute hydrochloric acid, filtered, washed with an aqueous solution of sodium carbonate, then with water, dissolved in dimethylformamide, and reprecipitated with water. After filtering, the precipitate was repeatedly washed with water, and dried under a reduced pressure. Four tenth grams of black powder were obtained.

Dehydrogenation with potassium permanganate. — To a solution of 1g. of potassium permanganate in 50 ml. of water were added 4~5ml. of concd. sulfuric acid, and then 0.5 g. of [III]. After stirring for 3 hours, the reaction mixture was filtered, washed with 5% aqueous solution of sodium carbonate, and refluxed with 100 ml. of water for an hour to remove water-soluble materials and dried in vacuo. (*Anal.* Found; Cl, 9.75).

Preparation of iodine-[III] complex. — Four tenth grams of [III] were suspended in a solution of 1.02 g. of iodine in 20 ml. of benzene, and the mixture was stirred at room temperature for 60 hours. The precipitate obtained was collected by filtration, and excess iodine was removed under 10 mm.Hg vacuo at 30°C for 8 hours. (*Anal.* Found ; halogen, 48.6).

Preparation of a trinitrobenzene-[IV] complex. — Four tenth grams of [IV] were suspended in a solution of 0.85 g. of trinitrobenzene in 20 ml. of benzene, and the mixture was stirred at room temperature for 5 hours. After filtering, the precipitate was refluxed with 20 ml. of benzene, filtered, and dried in vacuo. (*Anal.* Found ; halogen, 7.15).

Preparation of metal chelate compound. — (a) [V]-Cu²⁺: To a solution of 0.2 g. of [IV] in 25 ml. of dimethylformamide was poured a solution of 1 g. of copper acetate in 30 ml. of dimethylformamide, and 0.1 g. of black precipitate obtained was filtered, refluxed in 20 ml. of dimethylformamide, filtered, washed with a water-ethanol mixture, and dried in 10 mm.Hg vacuo at 60°C for 24 hours over P₂O₅. (b) [V]-miscellaneous metals : [V]-Zn²⁺, [V]-Pb²⁺ and [V]-Sn²⁺ were prepared with the similar method to

that of the preparation of [V]-Cu²⁺.

Analysis of the metal (See Table 4). — All samples, except [V]-Sn²⁺, were heated with fuming nitric acid at 250°C for five hours and the solutions obtained were analysed with the following method. The amount of Cu²⁺ was determined by gravimetric method. Pb²⁺ and Zn²⁺ were determined by EDTA-method.⁶⁾ [V]-Sn²⁺ was heated with concd. nitric acid, and Sn²⁺ was determined as SnO₂.

Measurement of the electrical conductivity. — The electrical conductivity of all compounds obtained above were measured. Fine powder of each compound was compressed into a disk (10 mm in diameter and 1~2 mm thick) under pressure of about 100k g/cm², and a thin cylinder formed was pasted on the both sides by a silver paster, connected with lead wire, dried with infrared irradiation. The dc measurement was performed employing dc amplifier under a dry nitrogen atmosphere. Each sample was rectified by the methods described above, and dried in 5 mm.Hg vacuo for a week over P₂O₅. The dc resistivity was measured in 3000 volt-cm⁻¹.

III. Results and Discussion

1) Reaction of 4,5-dichlorocyclohexene-3, 6-dione [I] with ammonia.

When ethanol was used as the solvent, the reaction product between [I] and ammonia was an infusible black powder, which contained halogen atoms, and was soluble in dimethylformamide, dimethylsulfoxide and an aqueous solution of sodium hydroxide. The halogen content of the powder precipitated in the course of the reaction was less than that of the product which was soluble in ethanol, as shown in Exp. 1, 2 of Table I. This seems to be due to the difference of the degree of

Table 1. Reaction of [I] or [III] with ammonia.

Exp. No.	Raw Material	Reaction Condition			Product					
		Solvent	Temperature (°C)	Time (hr.)	Colour	Yield (g.)	m.p. (°C)	Chlorine Content (%)	Nitrogen Content (%)	Abbreviation
1	I	C ₂ H ₅ OH	20	3	black-brown ^{a)}	23→11	>300	11.4	10.6	III
					" ^{b)}	23→3.5	"	16.3	—	—
2	"	"	"	"	"	25→4.5	"	10.6	—	—
3	III	D.M.F. ^{c)}	150	7	black	1→0.6	"	5.08	—	—
								(9.00) ^{b)}	—	—
4	"	"	150	8	"	1→0.5	"	4.9	—	—
5	"	"	200	10~12	"	1→0.8	"	2.3	15.5	VI

a) The weight of raw material.

b) The powder obtained after distilling the solvent.

c) Abbreviated for dimethylformamide.

polycondensation. As shown in Fig. 2, the infrared spectrum of the black powder is exhibited the absorption bands at 1555 cm⁻¹, 3100 cm⁻¹, which may correspond to —C=N and N—H absorption, respectively.

The ultraviolet spectrum of the black powder in dimethylformamide showed a

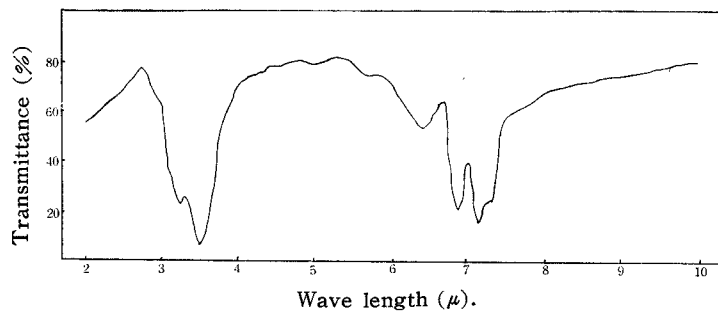


Fig. 2. I. R. Spectrum of [III].

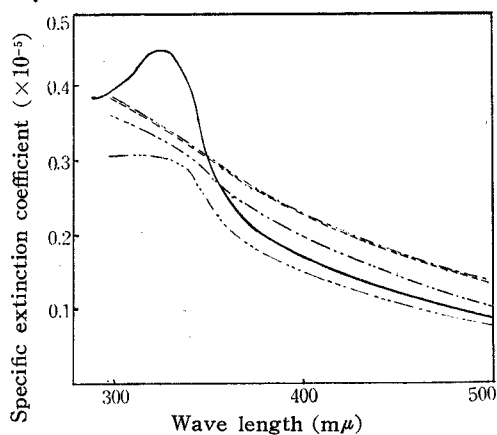


Fig. 3. U. V. Spectra of III, IV (N.B.S.)-D.M.F.,
 IV (PbO₂), IV (N.B.S.)-CD and IV (KMnO₄)
 —III, — — IV (N.B.S.)-D.M.F., ··· IV (PbO₂),
 -·-· IV (N.B.S.)-CD, —··— IV (KMnO₄).

strong absorption at 330 m μ , as shown in Fig. 3. The contents of nitrogen and chlorine were shown in Table I. The molecular weight of [III], which was estimated from the content of nitrogen, did not coincide with that calculated from the content of chlorine. These results of the spectrum and the analysis suggest that [I] reacts with ammonia to form [II] and then [II] enolizes to [III], which is a cross-conjugated compound. In an attempt to make ring-closure with condensation between two functional groups located in the middle or terminal part in a molecule, a further reaction of [III] with ammonia was carried out under the conditions shown in Table I. The product obtained after such treatment was infusible black powder and was insoluble in dimethylformamide, concd. aq. solution of sodium hydroxide and other organic solvents. The chlorine content of it was less than that of [III], on the other hand, the nitrogen content was more, as shown in Table I. These results suggested that intra- and/or inter-molecular ring closures and simultaneous dehydrogenations occurred repeatedly during the reaction of [III] with ammonia. If the ring closures completed, the product obtained had to have the formula as [VI], and to have a better heat-resistance than [III]. As shown in Fig. 4, the heat-resistance of [VI] was better than that of [III].

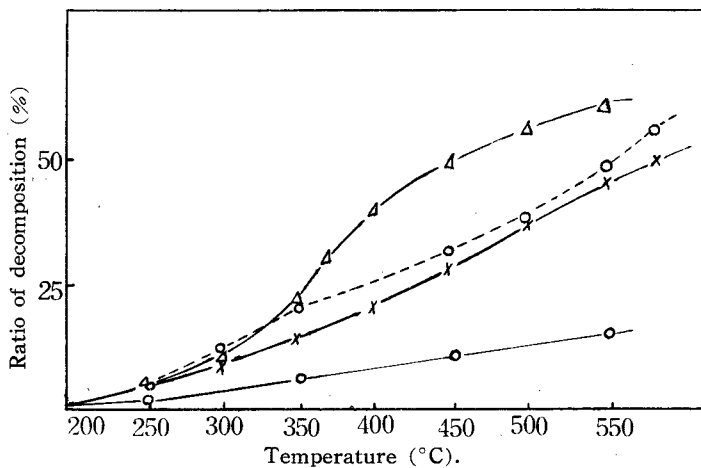


Fig. 4. Heat-resistance of III, IV (N. B. S.)-D.M.F., IV ($K_2Cr_2O_7$) and VI.
 — Δ — IV ($K_2Cr_2O_7$), $\cdots\circ\cdots$ III, — \times — IV (N.B.S.)-D.M.F. — \circ — VI.

2) Dehydrogenation.

[III] was dehydrogenated to [IV] with various conditions shown in Table 2. A treatment of [III] with N-bromosuccinimide in carbon tetrachloride increased the content of halogen.

Table 2. Dehydrogenation of [III].

Exp. No.	Raw Material	Oxidizing Reagent	Reaction Condition			Product				
			Solvent	Temperature (°C)	Time (hr.)	Yield (g.)	m.p. (°C)	Halogen Content (%)	Nitrogen Content (%)	Abbreviation
6	III	N.B.S. ^{a)} CH ₃ COOK	CCl ₄	76	1 (1) ^{b)}	0.5→0.3 ^{c)}	>300	25.4	6.96	IV(N.B.S.)- CCl ₄
7	"	"	CCl ₄ - D.M.F.	"	1 (1)	0.5→0.3	"	15.7	—	IV(N.B.S.)- CD
8	"	"	D.M.F.	"	0.5(1)	0.5→0.2	"	15.3	—	—
9	"	"	"	130	0.5 (0.5)	0.5→0.2	"	10.3	—	—
10	"	"	"	150	1(1.5)	"	"	6.9	10.73	IV(N.B.S.)- D.M.F.
11	"	"	"	"	2(2.5)	1→0.9	"	9.2	—	IV(N.B.S.)- Ins.
12	VI	"	"	130	0.5 (0.5)	0.8→0.7	"	4.9	11.95	—
13	III	Chloranil	CH ₃ C ₆ H ₅ CH ₃ - COOH	130-140	15	1→0.9	"	16.5	—	IV(chlor.)
14	"	PbO ₂	D.M.F.	150	8	0.5→0.4	"	5.68	—	IV(PbO ₂) ^{d)}
15	"	KMnO ₄ H ₂ SO ₄	H ₂ O	20	3	0.5→0.4	"	9.75	—	IV(KMnO ₄) ^{d)}
16	"	K ₂ Cr ₂ O ₇ H ₂ SO ₄	"	20-30	0.5	—	"	5.15	—	IV(K ₂ Cr ₂ O ₇) ^{d)}

a) Abbreviated for N-bromosuccinimide.

b) The time of a treatment with potassium acetate.

c) The weight of raw materials.

d) The contents of Pb²⁺ and Mn²⁺ were not detected, but the content of Cr³⁺ was 3.4%.

This result was not surprising in view of the incompleteness of the elimination of hydrogen bromide. The halogen content of the product obtained by the dehydrogenation in dimethylformamide was less than that of [III]. (Exp. 9, 10, 11, 12). However, the product precipitating in the course of the reaction in dimethylformamide at a higher temperature was insoluble in any organic solvent. (Exp. 11). The ultraviolet spectrum of the dehydrogenated product in dimethylformamide (Exp. 10) showed no evidence of absorption in $330m\mu$, as shown in Fig. 3. When chloranil was used as an oxidizing reagent, the ultraviolet spectrum of the product showed the same curve as that of [III]. In the case of lead peroxide, which was used generally as a dehydrogenating reagent for heterocyclic compounds containing nitrogen atom, the ultraviolet spectral characteristics of the product were similar to those in the case of the N-bromosuccinimide. The oxidation of [III] with potassium dichromate gave infusible black powder which was insoluble in any solvent, and in which a little of chromium ion was detected. The product of Exp. 10 (oxidizing reagent; N-bromosuccinimide) had a similar heat-resistance to that of [III], however, the product of Exp. 16 (oxidizing reagent; potassium dichromate) was less resistant to heat than [III].

3) Preparations of molecular complexes and metal chelate compounds.

Several molecular complexes of the dehydrogenated product (oxidizing reagent; N-bromosuccinimide) with iodine of various amounts were prepared with the method reported by Akamatu and coworkers⁴⁾ in the series of the studies of condensed polynuclear hydrocarbons. The [III] or [IV] (the dehydrogenated product of the [III] with N-bromosuccinimide) was dispersed in a solution of iodine in benzene, and the dispersed solution was stirred for about sixty hours at room temperature. During the stirring, some black powder precipitated gradually. Excess iodine which contaminated the precipitate was removed under vacuo at 30°C for long time. The contents of halogen in the molecular complexes obtained from [IV] or [VI] were larger than that obtained from [III], as shown in Table 3.

Table 3 Preparations of molecular complexes.

Exp. No.	Donor	Acceptor	Reaction Condition			Product			
			Solvent	Temperature ($^{\circ}\text{C}$)	Time (hr.)	Yield (g)	Halogen Content (%)	Weight of donor A mol. of iodine	Abbreviation
17	III	Iodine	C_6H_6	20	61	0.2→0.25	40.1	619.2	III-I ₂
18	IV (N.B.S.) -D.M.F.	"	"	"	5	0.5→0.4	25.6	1406.1	IV-I ₂ -L
19	"	Trinitrobenzene	"	"	"	0.5→0.5	7.15	—	IV-Tri.
20	"	Iodine	"	"	60	0.2→0.2	48.6	409.2	IV-I ₂ -M
21	VI	"	"	"	"	0.2→0.25	47.2	346.5	VI-I ₂

Some sorts of metal chelate compounds were prepared with the usual method.⁷⁾ The conditions for preparation and the analysis of the chelate compounds were shown in Table 4. The highest metal content was found in the case of Sn^{2+} chelate.

Table 4 Preparations of metal chelate compounds.

Exp. No.	Ligand	Metal salt	Solvent	Product				
				Colour	Metal Content (%)	Metal ^(a) mol. %	Weight of Ligand A mol. of iodine	Abbreviation
22	IV (N.B.S.) -D.M.F.	Cu(OAc) ₂	D.M.F. -H ₂ O	black	9.0	0.142	640.8	V-Cu ²⁺
23	"	Zn(OAc) ₂	"	"	10.9	0.166	536.7	V-Zn ²⁺
24	"	Pb(OAc) ₂	"	"	33.0	0.156	421.3	V-Pb ²⁺
25	"	SnCl ₂	"	"	36.0	0.303	211.2	V-Sn ²⁺

a) Metal mol. % is halogen content (%) / atomic weight of metal.

4) Electrical Conductivity.

Electrical conductivity of all compounds prepared above was shown in Table 5. Great care was taken to ensure the temperature equilibrium at measurement by slow

Table 5 Electrical conductivities of all compounds.

Compound ^{a)}	Temperature Range (°C)	Resistivity at 20°C (ohm-cm)	$\Delta\epsilon$ (eV.)
III	78~115	3×10^{15}	1.86
VI(150°C)	20.7~71	1.63×10^{11}	1.02
VI(200°C)	17~55	1.21×10^{11}	1.04
IV(N.B.S.)-D.M.F.	50~100	2.73×10^{14}	1.31
IV(N.B.S.)-Ins.	39~89	6.5×10^{12}	1.32
IV(Chlor.)	96~117	1.77×10^{18}	2.89
IV(PbO ₂)	20~30	4.3×10^{13}	—
IV(N.B.S.)-CCl ₄	62~100	1.12×10^{16}	1.90
IV(KMnO ₄)	96~135	2.3×10^{16}	1.95
IV(K ₂ Cr ₂ O ₇)	10~70	1.5×10^{13}	2.02
III-I ₂	7~29	8.7×10^9	1.90
IV-I ₂ -L	51~63.5	6.5×10^{13}	1.38
IV-Tri.	76~100	6.0×10^{14}	1.61
IV-I ₂ -M	9.7~36.7	1.38×10^8	1.84
VI-I ₂	18	5.2×10^7	—
V-Cu ²⁺	25~99.2	4.5×10^{13}	1.43
V-Zn ²⁺	58~102	6.55×10^{13}	1.31
V-Pb ²⁺	35~106	8.1×10^{12}	1.27
V-Sn ²⁺	27~60	1.17×10^{12}	1.44

a) Each compound was indicated by an abbreviation.

raising and lowering of temperature. A linear relationship between $\log_{10} \rho$ (ρ ; electrical resistivity in ohm-cm). and $1/T$ (T ; absolute temperature) was observed at an ascending and a descending temperature and there was no hysteresis for all compounds. Fig. 5 represents this linear relationship with some compounds as example.

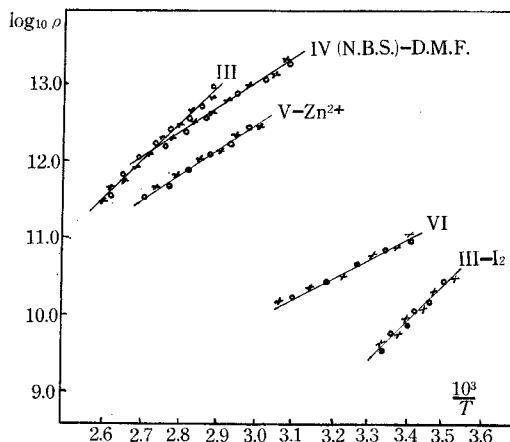


Fig. 5 Relationships between $\log_{10} \rho$ and $1/T$ for III, IV(N.B.S.)-D.M.F., VI, III-I₂ and V-Zn²⁺.

- × Ascending temperature.
- Descending temperature.

From this relation, the following equation was confirmed.

$$\rho = \rho_0 \exp(\Delta\epsilon/2kT)$$

where, $\Delta\epsilon$ is an apparent energy gap, k is the Boltzmann constant and ρ_0 is a specific electrical resistivity. The range of temperature at measurement, the values of $\Delta\epsilon$, and ρ_{20} (at 20°C) were given in Table 5. ρ_{20} and $\Delta\epsilon$ of [III] were of the order of 10^{15} ohm-cm. and 1.8 eV., respectively, whereas those of [VI] were 10^{11} ohm-cm and 1.01 eV. Among the products dehydrogenated with N-bromosuccinimide, those of low halogen content showed the low values of ρ_{20} and $\Delta\epsilon$. In the case of the oxidation with chloranil or potassium permanganate, ρ_{20} and $\Delta\epsilon$ were similar to those of [III]. The conductivity of the compound which was obtained by the oxidation of [III] with lead peroxide coincided comparatively well with that of the compound which was obtained by the oxidation of [III] with N-bromosuccinimide. These suggested that the number of π electron in [IV] and [VI] was larger than that of [III].

ρ_{20} of molecular complexes with iodine was smaller than that of other compounds by a factor of at least $10^6 \sim 10^7$. Thus, the complexes between polybenzopyrazine and iodine have a very good electrical conductivity, as found in a series of condensed polynuclear hydrocarbons. Though the conductivities of Sn²⁺- and Pb²⁺- chelate were the best among those of metal chelate compounds, the effect of the chelation was not so remarkable as expected.

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